ABSTRACT: Superconcentrated electrolytes for lithium-ion batteries have shown promise in circumventing certain limitations of conventional carbonate electrolytes at lower concentrations while introducing new challenges such as decreased conductivity. We use molecular dynamics simulations with diffusion and residence time analyses to elucidate the main modes of transport of LiPF$_6$ and LiBF$_4$ in propylene carbonate at concentrations ranging from 1 to 3 M. Notably, we find that the Li$^+$ mode of diffusion with respect to its surrounding propylene carbonate solvation shell is a mix of vehicular and structural diffusion at all studied concentrations, exhibiting a small increase toward structural diffusion in the superconcentrated regimes. Furthermore, and important for future strategies toward improved conductivity, we find that the Li$^+$ ions associated with PF$_6^-$ anions move in an increasingly vehicular manner as the salt concentration is increased, while the Li$^+$ ions associated with BF$_4^-$ anions move in an increasingly structural manner.

The liquid electrolyte of lithium-ion batteries (LIBs) provides a medium for ionic charge transport between the electrodes and effectively sets the window of electrochemical stability. Superconcentrated electrolytes for LIBs (~3 M) received attention as early as 1985 and generally include both nonaqueous organic systems as well as aqueous electrolytes such as 3 M LiPF$_6$ in propylene carbonate (PC) or 21 M LiTFSI “water-in-salt.” Currently, both superconcentrated LiPF$_6$ in PC and superconcentrated LiBF$_4$ in PC (the latter with an added diluent) are under investigation as “state-of-the-art” electrolytes for LIBs. Interest in these systems stems from a combination of improved properties such as increased oxidative stability, absence of exfoliation, low volatility, higher charge density, and improved charge transfer kinetics. However, these potential advantages are not without drawbacks, as the cost of the salt is considerable, the viscosity may be dramatically increased, and the conductivity reduced. The impaired conductivity presents a fundamental flaw in particular, and considerable effort has been devoted to understanding the atomistic motifs for ionic conductivity in these complex, nondilute solutions with the aim to suggest possible improvements. Both structural as well as dynamic measurements have been employed, including nuclear magnetic resonance (NMR), infrared spectroscopy (IR), dielectric spectroscopy, and conductometric analysis as well as computational methods based on extensions of the mean spherical approximation (MSA) theory and molecular dynamics simulations. However, despite the considerable body of work, there is no consensus on the molecular-level mechanisms of charge transport in superconcentrated aprotic electrolytes. Yamada and Yamada suggested that structural diffusion of Li$^+$ may become the main transport mode as concentration is increased, perhaps due to a “repeated ion dissociation/association process”, as opposed to vehicular-type mechanisms that should dominate at lower concentrations. Such ion hopping processes are often referred to as Groththus-type, where the hopping here refers to intersalt events, unlike the Groththus-type processes that directly involve charge transfer to and from the solvent. Specifically for LiPF$_6$ in PC, Hwang et al. found via spectroscopy that contact dimers contribute to decreased conductivity in the high concentration regime and that the remaining conductivity is attributed to solvent separated ion pairs (SSIPs) and solvent separated dimers (SSDs). These authors found no support for any Groththus-type ionic transport mechanism for LiPF$_6$ but suggested that Groththus-type diffusion may be a possibility for LiBF$_4$ in PC in superconcentrated regimes. Adding to the debate regarding LiPF$_6$ in PC, Kondo et al. reported negligible ion-pairing (<20 %) via conductometric analysis even at high concentrations (˃3 M). Hence, clarification of atomic level transport mechanisms is of immediate interest. In this work, we report the solvation

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structure and diffusion constants of LiPF₆ in PC and LiBF₄ in PC for a range of concentrations spanning 1–3 M. We compare the obtained values to previously reported experiments and, using residence time and bound time analysis, recover the characteristic diffusion length scales, allowing for a thorough characterization of the transport modes for the respective salt components Li⁺, PF₆⁻, and BF₄⁻ as a function of concentration.

To qualify the main mode of diffusion of a species i relative to another species j, the characteristic diffusional length scale \(L_{ij}^\text{cutoff}\) can be obtained from the diffusion constant of a species \(D_i\) and residence time between two species \(\tau_{ij}^\text{res}\) via the following relationship:

\[
L_{ij}^\text{cutoff} = \sqrt{6D_{ij}^\text{cutoff}}
\]  

(1)

The main mode of diffusion can be simply determined by comparing \(L_{ij}^\text{cutoff}\) to the length scale relevant to the solvation shell \(L^5\). Provided a judicious choice of \(L^5\) is made, which we discuss later, the following criteria can be employed:

\[
\begin{align*}
L_{ij}^\text{cutoff} &> L^5 & &\text{vehicual motion} \\
L_{ij}^\text{cutoff} &< L^5 & &\text{structural diffusion}
\end{align*}
\]  

(2)

Under vehicular transport, the species in question diffuses appreciably with its neighbors. Figure 1a shows one cartoon example where a tightly bound solvation shell diffuses as one species. In structural diffusion, the neighboring species do not diffuse together by any appreciable amount, as illustrated in Figure 1b. For example, the neighboring solvents are frequently exchanged as the solvated species diffuses with its shell or the species undergoes some type of hopping or Groththus-type mechanism. In Figure 1c, a mix of structural-and vehicular-type diffusion is shown, where a solvent is lost as the ion diffuses a distance comparable to the size of a solvation shell, while the remaining fraction of the solvation shell diffuses as a single kinetic entity.

\(D_b\) for both ions and solvent, can be obtained for a closed and thermally equilibrated liquid electrolyte system from the Einstein relation, provided the position \(x_i\) of species \(i\) is known as a function of time:

\[
D_i = \lim_{t \to \infty} \frac{1}{6t} \left( \frac{1}{N_i} \sum \left( x_i(t) - x_i(0) \right)^2 \right)
\]  

(3)

To determine the residence time \(\tau_{ij}^\text{res}\), or the average time species i and j travel together as neighbors before separating, and subsequently extract a diffusion mechanism, it is necessary to define the relevant length scales for diffusion in the system. Two species (e.g., Li⁺ and PC) are classified as direct neighbors if they are separated by a distance cutoff \(L_{ij}^\text{cutoff}\). In this work, \(L_{ij}^\text{cutoff}\) is taken to be the minimum after the first peak of the relevant radial distribution function \(g(r)\). The sizes of solvation shells, \(L^5\), or alternatively, the distance between two solvation sites, is here shown in Table 1. Further details are provided in the Supporting Information.

### Table 1. Size of Cutoff \(L_{ij}^\text{cutoff}\) for Determination of Residence Times \(\tau_{ij}^\text{res}\) and Estimate of Solvation Shell Size \(L^5\) between Two Species

<table>
<thead>
<tr>
<th></th>
<th>Li⁺-PC (Å)</th>
<th>Li⁺-PF₆⁻ (Å)</th>
<th>Li⁺-BF₄⁻ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L_{ij}^\text{cutoff})</td>
<td>3.2</td>
<td>4.6</td>
<td>4.1</td>
</tr>
<tr>
<td>(L^5)</td>
<td>6.6</td>
<td>4.6</td>
<td>4.1</td>
</tr>
</tbody>
</table>

A residence time function \(H(t)\) can be established such that \(H(t)\) is unity if the two species are within \(L_{ij}^\text{cutoff}\) of each other and zero otherwise:

\[
H_{ij}(t) = \begin{cases} 
1, & \text{if } x_i(t) - x_j(t) < L_{ij}^\text{cutoff} \\
0, & \text{otherwise}
\end{cases}
\]  

(4)

The autocorrelation function of \(H(t)\) can be then calculated:

\[
\xi_{ij}(t) = \langle H_{ij}(t)H_{ij}(0) \rangle
\]  

(5)

From the autocorrelation function \(\xi_{ij}(t)\), a biexponential fit allows for inspection of the residence time \(\tau_{ij}^\text{res}\) defined via the following relationship:

\[
\xi_{ij}(t) = a \exp\left(\frac{-t}{\tau_{ij}^\text{res}}\right) + (1 - a) \exp\left(\frac{-t}{\tau_{ij}^\text{short}}\right)
\]  

(6)

In eq 6, \(a\), \(\tau_{ij}^\text{res}\), \(\tau_{ij}^\text{short}\), and \(\beta\) are fitting parameters. The second term with \(\tau_{ij}^\text{short}\) is ascribed to processes deemed subdiffusive, while the first term is relevant to the time scale of the diffusion process(es). \(\beta\), the exponential stretch parameter (0 < \(\beta\) < 1), would deviate from unity as various diffusion modes of different time scales contribute to \(\xi_{ij}(t)\). We note that this equation is similar to that used by Borodin and Smith and Dong et al. for residence time analysis, where only the first term from the right-hand side is included: for \(t \gg \tau_{ij}^\text{short}\), their employed equation is recovered. The more elaborate eq 6 is used here as the previous approximation does not explicitly

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Figure 1. Cartoon illustration of diffusion of (a) vehicular quality, (b) structural quality, and (c) a mix of structural and vehicular quality. O, C, H, and Li atoms are shown as red, gray, white, and purple, respectively.
yield a measure of the short time scales implied by including the fit from the first (stretched exponential) term alone. Thus, with eqs 1, 3, and 6, the condition in eq 2 qualifies the main diffusional mode of a species as either structural or vehicular. Note that the computed $L^n_s$ will depend on which species is assigned as species $i$ and which is species $j$, i.e. which species' diffusion coefficient is used in eq 1. Here, we choose Li$^+$ to be species $i$ for all analyses.

As Li$^+$ diffuses, it may move from one solvation shell with a counterion to another solvation shell with a different counterion. A measure of the time Li$^+$ spends around at least one counterion is the bound time $\tau_{\text{bound}}$.8 If the cation "hops" from one anion to another, it remains bound through multiple residence times for a total time $\tau_{\text{bound}}$. Such a measure is deemed useful to determine "ionic-hopping" behavior. $\tau_{\text{bound}}$ was calculated using the average time the primary solvation shell of a Li-ion includes at least one anion with a smoothing function which removes events on a time scale smaller than $\tau_{\text{PC}}$ to avoid including subdiffusive events.

Molecular dynamics simulations were carried out with GROMACS (GROningen MAchine for Chemical Simulations).29 Initial configurations were packed with PACKMOL in box sizes of $5 \times 5 \times 5$ nm$^3$.30 Five different concentrations between 1.0 and 3.6 M were studied for both LiPF$_6$ in PC and LiBF$_4$ in PC, respectively. Production runs were 50 ns for the two lowest concentrations and at least 100 ns for the three highest concentrations. These were under the isothermal–isobaric ensemble using a Parinello-Rahman barostat (4000 fs relaxation) with a velocity rescaling thermostat (1000 fs relaxation) with a 2 fs time step of integration for the equations of motion. The diffusion constants were obtained by inspecting the linear regime of the time-averaged mean squared displacement of all relevant moieties (see Supporting Information for further details). Diffusion constants of Li$^+$, PF$_6^-$, and PC were calculated in this work using eq 3.

For the force field parameters for PC and Li$^+$ were taken from the standard OPLS force field, while those for PF$_6^-$ are taken from Lopez and Padua and BF$_4^-$ from Doherty et al.36 Atom type identification and partial charge assignments for PC were automated using the Macromodel software package, which generates charges based on the OPLS force field defaults using the bond-charge increment formalism. Ionic charges for Li$^+$ and PF$_6^-$ were scaled by 0.8 as default charges ($\pm 1.0$) have been shown to typically overestimate interionic interactions in nonpolarizable force fields.39,40 We note previous work on MD simulations of LiPF$_6$ and LiBF$_4$ at conventional concentrations (1 M) which have not scaled down ionic charges have underestimated diffusivity constants by an order of magnitude, as well as overestimated ionic correlations.12 Preceding the production runs, initial equilibrations were undertaken with a steepest descent, conjugate gradient minimization, followed by an isothermal–isobaric (T = 298 K, P = 1 atm) equilibration with the Berendsen barostat for 5 ns duration. Duplicate production runs were undertaken for all concentrations, and error bars report the standard error of the two duplicates.

Figure 2a shows the solvent coordination number (CN) of Li$^+$ as a function of salt concentration. Analyzing CN informs us of solvation structure. Experimental values based on IR measurements from various groups for PC-LiPF$_6$ and PC-LiBF$_4$ have been plotted for comparison.6,14,42 The exact coordination number of Li$^+$ in carbonate solutions is the subject of ongoing investigation, and for similar concentrations can vary depending on the method of investigation by numbers of $3^{4,5,41}$ Our simulation results agree within 2 of the coordination numbers of Nie et al. and Hwang et al. across various concentrations.6,14 Intuitively, the coordination number decreases with concentration due to the increased number of neighboring anions as concentration is increased,52 in agreement with the experimental trends. Li$^+$ in the LiBF$_4$ solution shows lower average coordination numbers due to increased ion-pairing over LiPF$_6$. Figures 2b and 2c show the average number of anionic neighbors of Li$^+$ and which is species $i$, $j$, and $n$.
solvation shell) are favored. This strictly structural criterion does not properly consider whether or not ionic species form well-defined chemical entities with other ionic neighbors or alternatively exist as associated for a non-negligible duration in time. Such limitations of the strictly static criteria are overcome via a dynamical analysis such as those of ionicity (or Haven ratio), previously undertaken by Takeuchi et al., or analysis of the short-time diffusion mechanisms induced by ion complexation. In this work, we undertake residence time analysis to investigate this dynamical behavior. Both ionicity and residence time analysis have been also used to study ionic liquids, for which the aforementioned descriptions of ion correlation may be more apt than concepts of ion-pairing inferred via static structural measurements in dilute regimes.

To validate the dynamics of the simulations, diffusion constants were computed and compared to experiment. Figure 3 (top row) shows the computed diffusion constants as a function of concentration for the ionic species. The diffusion constants of all species decrease with increased salt concentration. However, there is a more pronounced decrease in the diffusion constant for the anions (PF$_6^-$ or BF$_4^-$) than for Li$^+$. Thus, the ratio of $D_{Li^+}$, sometimes referred to as the transport number, increases from 1 to 3 M. This trend is consistent with the experimentally reported values. Figure 3 (bottom row) shows the PC solvent diffusion constant as a function of concentration. The diffusion constants for all three electrolyte species (Li$^+$, PF$_6^-$ or BF$_4^-$, and PC) computed here are in fair agreement with the experimental results previously published. Hence, we surmise that the dynamics are well-reproduced by our models, which allows us to proceed to the residence time analysis.

Figure 4 (top panel) shows the residence time $\tau_{res}$ for various species and (middle panel) $L^c$ as a function of concentration. (bottom panel) $L_{PC}$. Error bars, when smaller than the symbols for computed data, are not shown.

Figure 3. Diffusion constants as a function of salt concentration for ionic species (Li$^+$, PF$_6^-$, and BF$_4^-$) (top row) and PC (bottom row) for LiPF$_6$ in PC (left column) and LiBF$_4$ in PC (right column). Experimental values are taken from the literature. Error bars, when smaller than the symbols for computed data, are not shown.

Figure 4. (top panel) Residence time $\tau_{res}$ for various species and (middle panel) $L^c$ as a function of concentration. (bottom panel) $L_{PC}$. Error bars, when smaller than the symbols for computed data, are not shown.

calculation of $L_{PC}^c$ via eq 1. Figure 4 (middle panel) shows $L_{PC}^c$ as a function of concentration. $L_{Li^+-PC}^c$ indicates that the transport mode of Li$^+$ with PC for both anions is only slightly vehicular, and arguably mixed, as the solvent shell exchanges one of its comprising solvent molecules as the Li$^+$ diffuses a distance slightly above a solvation shell size $L^S$ (e.g., $L_{Li^+-PC}^c \approx 1.4$ at 1.0 M). At 1.0 M, Borodin and Smith found a similar result for LiTFSI in ethylene carbonate (i.e., $L_{Li^+-PC}^c \approx 1$), noting that this result is contrary to conventional expectation. For all concentrations studied here, the Li$^+$ diffusion mode with respect to PC increases to slightly more structure diffusion-type as concentration increases.
The average transport mode of Li\(^+\) with respect to neighboring PF\(_6^-\) at 1.0 M is a near equal mix of structural and vehicular motion (\(\frac{L^c}{\tau^c} \approx 1\)). However, as concentration is increased, the vehicular quality is significantly increased. This is in agreement with the experimental observation that the ionicity of LiPF\(_6\) decreases with increasing concentration,\(^{12}\) where positive and negative ions show a higher degree of correlation in their motion.

Analysis of the diffusion mode of Li\(^+\) with respect to BF\(_4^-\) reveals that \(L^c_{\text{Li}^+-\text{BF}_4^-}\) is significantly larger than \(L^c_{\text{Li}^+-\text{PF}_6^-}\) in the studied concentration range, or more vehicular. In other words, a Li\(^+\) will travel on average further with a BF\(_4^-\) than a PF\(_6^-\). This can be rationalized by the stronger binding energy between Li\(^+\) and BF\(_4^-\) than Li\(^+\) and PF\(_6^-\), a trend which has been observed previously using both experimental conductivity measurements\(^{36}\) and quantum chemical calculations in carbonate blends.\(^{57}\) Moreover, the concentration trends are different for LiBF\(_4\) and LiPF\(_6\); \(L^c_{\text{Li}^+-\text{BF}_4^-}\) decreases while \(L^c_{\text{Li}^+-\text{PF}_6^-}\) increases with concentration. This indicates that the diffusion of Li\(^+\) with BF\(_4^-\) is increasingly structural with increasing concentration. We speculate that the reason for this is due to the fact that Li\(^+\) in the LiBF\(_4\) system on average holds more anions in its solvation shell (see Figures 2b and c), and a Li\(^+\) may interact more strongly to an anion if it is the only anion in its primary solvation shell.

To further characterize the mode of transport, bond time analysis was employed. As defined above, \(\tau^\text{bound}\) is a measure of the time spent by Li\(^+\) around at least one counterion, and a higher ratio of \(\frac{\tau^\text{bound}}{\tau^\text{res}}\) indicates a higher likelihood of ion-hopping. Figure 4 (bottom) shows \(\frac{\tau^\text{bound}}{\tau^\text{res}}\) versus concentration. The similar trends show that \(\frac{\tau^\text{bound}}{\tau^\text{res}}\) increases above 1.5 M for both LiPF\(_6\) and LiBF\(_4\) solutions. We cautiously label such behavior as increasingly “ion-hopping”-type, where the Li\(^+\) more often moves directly between different anions without entering an intermediate, fully solvated state. We note that in the electrolytes studied here, the solvation sites are not fixed as in PEO\(^{9,65}\) or polyelectrolytes.\(^{28,60}\) Across concentrations, \(\frac{\tau^\text{bound}}{\tau^\text{res}}\) is comparable for LiBF\(_4\) and LiPF\(_6\), indicating that similar ion-hopping behavior increase is seen for both systems. This is likely due to nonspecific bulk concentration effects. Thus, with regards to neighboring counterions, the differences in transport between LiPF\(_6\) and LiBF\(_4\) solutions are not in the ion-hopping behavior but between the distance traveled by a Li\(^+\) before an anion is exchanged, and how that distance changes with concentration (increases to become more vehicular for LiPF\(_6\) and decreases to become more structural for LiBF\(_4\)). Furthermore, we note that at high concentrations, the conductivity of LiBF\(_4\) in PC overtakes that of LiPF\(_6\) in PC,\(^{13}\) which we speculate as due to the change in mode of diffusion. Further investigation of this effect is subject of future work.

In summary, we report the solvation structure, diffusion constants, and main transport mechanisms of LiPF\(_6\) and LiBF\(_4\) in PC for a range of concentrations spanning 1–3 M. While there is a small increase in structural diffusion quality for the positive charge carrier Li\(^+\) with respect to the solvent, its main mode of transport remains mixed-vehicular even at 3 M for both LiPF\(_6\) in PC and LiBF\(_4\) in PC systems. These results challenge previous beliefs which hold that the transport mode of Li\(^+\) with respect to the solvent should be predominantly structural at high concentrations.\(^2\) Moreover, via residence time analysis, we find that the transport of Li\(^+\) with respect to the counterion is significantly different, namely more vehicular, for BF\(_4^-\) over PF\(_6^-\). Although the ion-hopping quality of Li\(^+\) with respect to the counterion is comparable between LiBF\(_4\) and LiPF\(_6\) solutions as concentration is increased, Li\(^+\) with respect to BF\(_4^-\) shows a shift toward more structural-type diffusion, in contrast to LiPF\(_6\), which shows more vehicular-type. We hope that our work may be used to inform and explore viable paths forward to enhance and explore the transport of Li\(^+\) in superconcentrated PC electrolytes. For example, low viscosity cosolvents, which may be used to enhance hydrodynamic properties, remain to be investigated in their effect on diffusion mechanisms.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.9b02118.

Additional details on the simulations and analysis (PDF)

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